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(54) LARGE-SIZE CASTING MADE OF COLUMNAR CRYSTAL NI-BASED HEAT RESISTANT ALLOY, EXCELLENT IN HIGH TEMPERATURE INTERGRANULAR CORROSION RESISTANCE

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a large-size casting made of columnar crystal Ni-based heat resistant alloy for turbine blade, usable as turbine blade for gas turbine.
SOLUTION: This casting has a composition consisting of 12.0-14.3% Cr, 8.5-11.0% Co, 1.0-3.5% Mo, 3.5-6.2% W, 3.0-5.5% Ta, 3.5-4.5% Al, 2.0-3.2%, Ti, 0.04-0.12% C, 0.005-0.05% B, 0.001-5ppm Zr, and the balance Ni with inevitable impurities and further containing, if necessary, one or ≥2 kinds among the following (a) and (b): (a) 0.5-100ppm of Mg and/or Ca; (b) one or ≥2 kinds among 0.02-0.5% Pt, 0.02-0.5% Rh, and 0.02-0.5% Re.

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CLAIMS

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(57) [Claim(s)]
[Claim 1] By weight %, Cr:12.0-14.3%, Co:8.5-11.0%, Mo: 1.0-3.5%, W:3.5 - 6.2%, Ta:3.0-5.5%, aluminum: 3.5-4.5%, Ti:2.0-3.2%, C:0.04 - 0.12%, The columnar crystal nickel radical heat-resistant-alloy large-sized casting excellent in the intergranular corrosion-proof [elevated-temperature] nature characterized by having the presentation which Zr:0.001-5ppm are contained and the remainder becomes from nickel and an unescapable impurity B:0.005 to 0.05%.
[Claim 2] By weight %, Cr:12.0-14.3%, Co:8.5-11.0%, Mo: 1.0-3.5%, W:3.5 - 6.2%, Ta:3.0-5.5%, aluminum: 3.5-4.5%, Ti:2.0-3.2%, C:0.04 - 0.12%, Zr:0.001-5ppm are contained B:0.005 to 0.05%. The columnar crystal nickel radical heat-resistant-alloy large-sized casting excellent in the intergranular corrosion-proof [elevated-temperature] nature characterized by having the presentation which Mg and/or calcium:0.5-100ppm are furthermore contained, and the remainder becomes from nickel and an unescapable impurity.
[Claim 3] By weight %, Cr:12.0-14.3%, Co:8.5-11.0%, Mo: 1.0-3.5%, W:3.5 - 6.2%, Ta:3.0-5.5%, aluminum: 3.5-4.5%, Ti:2.0-3.2%, C:0.04 - 0.12%, Zr:0.001-5ppm are contained B:0.005 to 0.05%. The columnar crystal nickel radical heat-resistant-alloy large-sized casting excellent in the intergranular corrosion-proof [elevated-temperature] nature characterized by having the presentation which 1 of Pt:0.02-0.5%, Rh:0.02-0.5%, and Re:0.02-0.5% of sorts and two sorts or more are furthermore contained, and the remainder becomes from nickel and an unescapable impurity.
[Claim 4] By weight %, Cr:12.0-14.3%, Co:8.5-11.0%, Mo: 1.0-3.5%, W:3.5 - 6.2%, Ta:3.0-5.5%, aluminum: 3.5-4.5%, Ti:2.0-3.2%, C:0.04 - 0.12%, Zr:0.001-5ppm are contained B:0.005 to 0.05%. Furthermore, Mg and/or calcium:0.5-100ppm are contained. Further Pt:0.02-0.5%, Rh: The columnar crystal nickel radical heat-resistant-alloy large-sized casting excellent in the intergranular corrosion-proof [elevated-temperature] nature characterized by having the presentation which 1 of 0.02-0.5% and Re:0.02-0.5% of sorts and two sorts or more are contained, and the remainder becomes from nickel and an unescapable impurity.
[Claim 5] The large-sized turbine blade characterized by consisting of a columnar crystal nickel radical heat-resistant-alloy casting excellent in intergranular corrosion-proof [elevated-temperature] nature according to claim 1, 2, 3, or 4.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the large-sized turbine blade used as turbine ** and **** of the gas turbine which consisted of columnar crystal nickel radical heat-resistant-alloy castings which were especially excellent in intergranular corrosion-proof [elevated-temperature] nature, and a bucket of an elevated-temperature blower about the columnar crystal nickel radical heat-resistant-alloy large-sized casting excellent in intergranular corrosion-proof [elevated-temperature] nature.
[0002]
[Description of the Prior Art] It is just going to be known that turbine ** and **** of a gas turbine, and the bucket of an elevated-temperature blower consist of nickel radical heat-resistant-alloy castings. To JP,6-57395,A It is weight % (% hereafter) as a nickel radical heat-resistant alloy for making turbine ** and **** of a gas turbine, and the bucket of an elevated-temperature blower. weight % -- being shown -- (a) Cr:13.1-15.0% and Co: -- 8.5 to 10.5% Mo: 1.0-3.5%, W:3.5 - 4.5%, Ta:3.0-5.5%, aluminum: 3.5-4.5%, Ti:2.0-3.2%, C:0.06 - 0.12%, B:0.005 - 0.025%, Zr:0.010-0.050%, Contain Mg and/or calcium:1-100ppm and have the presentation which the remainder becomes from nickel and an unescapable impurity. nickel radical heat-resistant alloy excellent in high temperature strength, elevated-temperature oxidation resistance, and elevated-temperature corrosion resistance, (b) Cr:13.1-15.0%, Co:8.5-10.5%, Mo:1.0-3.5%, W:3.5 - 4.5%, Ta:3.0-5.5%, aluminum:3.5-4.5%, Ti: 2.0-3.2%, C:0.06 - 0.12%, B:0.005 - 0.025%, Hf:0.2-1.5% is contained further 0.010 to 0.050%. Zr: -- Contain Mg and/or calcium:1-100ppm and have the presentation which the remainder becomes from nickel and an unescapable impurity. nickel radical heat-resistant alloy excellent in high temperature strength, elevated-temperature oxidation resistance, and elevated-temperature corrosion resistance, (c) Cr:13.1-15.0%, Co:8.5-10.5%, Mo:1.0-3.5%, W:3.5 - 4.5%, Ta:3.0-5.5%, aluminum:3.5-4.5%, Ti: 2.0-3.2%, C:0.06 - 0.12%, B:0.005 - 0.025%, Mg and/or calcium:1-100ppm are contained Zr:0.010-0.050%. Hf:0.2-1.5% is contained. Further Furthermore, Pt:0.02-0.5%, 1 of Rh:0.02-0.5% and Re:0.02-0.5% of sorts and two sorts or more are contained. nickel radical heat-resistant alloy excellent in the high temperature strength, elevated-temperature oxidation resistance, and elevated-temperature corrosion resistance which have the presentation which the remainder becomes from nickel and an unescapable impurity, (d) Cr:13.1-15.0%, Co:8.5-10.5%, Mo:1.0-3.5%, W:3.5 - 4.5%, Ta:3.0-5.5%, aluminum:3.5-4.5%, Ti: 2.0-3.2%, C:0.06 - 0.12%, B:0.005 - 0.025%, Mg and/or calcium:1-100ppm are contained Zr:0.010-0.050%. Furthermore, Hf:0.2-1.5% is contained. Further Pt:0.02-0.5%, Rh: 1 of 0.02-0.5% and Re:0.02-0.5% of sorts and two sorts or more are contained, and nickel radical heat-resistant alloy excellent in the high temperature strength, elevated-temperature oxidation resistance, and elevated-temperature corrosion resistance which have the presentation which the remainder becomes from nickel and an unescapable impurity etc. is indicated.
[0003] On the other hand, it is also known that turbine ** and **** of a gas turbine, and the bucket of an elevated-temperature blower consist of columnar crystal nickel radical heat-resistant-alloy castings. In order to manufacture this columnar crystal nickel radical heat-resistant-alloy casting, usual one direction coagulation equipment is used. nickel radical alloy molten metal which carried out vacuum suction of the inside of a vacuum chamber, and was dissolved with the fusion furnace in this one direction coagulation equipment After pouring into the mold which fixed on the chill plate and was heated in temperature of 1480-1530 degrees C, A chill plate is pulled down through water-cooled chilling, mold is caudad pulled down by rate:200 - 350 mm/h, and a long columnar crystal nickel radical heat-resistant-alloy casting is manufactured by growing up the columnar crystal formed in the chill plate.
[0004]

[Problem(s) to be Solved by the Invention] In recent years, the turbine blade installed there is also enlarged with enlargement of a gas turbine. However, when the large-sized turbine blade which consists of a columnar crystal nickel radical heat-resistant-alloy casting, especially a columnar crystal nickel radical heat-resistant-alloy casting with the conventional nickel radical heat-resistant alloy was manufactured, crystal grain made it big and rough, the segregation of an alloy content became large, from the place where intergranular corrosion advances remarkably, intergranular corrosion-proof [elevated-temperature] nature fell substantially and the dependability and the life of a large-sized turbine blade which consist of a columnar crystal nickel radical heat-resistant-alloy casting were falling in the largest grain boundary of a component segregation.

[0005]

[Means for Solving the Problem] Then, as a result of inquiring wholeheartedly so that this invention person etc. may raise the intergranular corrosion-proof [elevated-temperature] nature of a large-sized turbine blade, the amount of Zr added into nickel radical alloy is restricted to ultralow volume. Cr: 12.0-14.3%, Co:8.5-11.0%, Mo:1.0-3.5%, W:3.5 - 6.2%, Ta:3.0-5.5%, aluminum:3.5-4.5%, Ti: 2.0-3.2%, C:0.04 - 0.12%, B:0.005 - 0.05%, Contain Zr:0.001-5ppm and it limits to the presentation which the remainder becomes from nickel and an unescapable impurity. A chill plate is pulled down pouring into the mold of one direction coagulation equipment the molten metal obtained by dissolving nickel radical alloy of this presentation. The obtained columnar crystal nickel radical heat-resistant-alloy casting at 1180-1265 degrees C 900 to 1600 atmospheric pressure, Give HIP of maintenance for 1 to 5 hours, and solution heat treatment of 1200-1265-degree C 2 - 5-hour maintenance at an elevated temperature is performed rather than before. If aging heat treatment of maintenance is performed at 760-870 degrees C for 16 to 24 hours after holding at further 950-1080 degrees C for 2 to 10 hours The columnar crystal nickel radical heat-resistant-alloy casting which was excellent in intergranular corrosion-proof [elevated-temperature] nature conventionally was obtained, and the large-sized turbine blade which consists of a columnar crystal nickel radical heat-resistant-alloy casting excellent in this intergranular corrosion-proof [elevated-temperature] nature carried out the knowledge of having the property which was excellent in intergranular corrosion-proof [elevated-temperature] nature conventionally, and resulted in this invention.

[0006] This invention is made based on this knowledge. (1) Cr:12.0-14.3%, Co: 8.5-11.0%, Mo:0.5-4%, W:3.5 - 6.2%, Ta: 3.0-5.5%, aluminum:3.5-4.5%, Ti:2.0-3.2%, C:0.04 - 0.12%, and B:0.005 to 0.05%, Zr:0.001-5ppm are contained and it has the description in the columnar crystal nickel radical heat-resistant-alloy large-sized casting excellent in the intergranular corrosion-proof [elevated-temperature] nature which has the presentation which the remainder becomes from nickel and an unescapable impurity.

[0007] The component presentation of nickel radical alloy which constitutes the columnar crystal nickel radical heat-resistant-alloy large-sized casting excellent in the intergranular corrosion-proof [elevated-temperature] nature of this invention By weight %, Cr:13-14%, Co:9.4-10.6%, Mo:1.2-2.0%, It is much more desirable that contain Zr:0.01-1ppm and the remainder consists of nickel and an unescapable impurity W:4.2 - 5.8%, Ta:4.0-5.2%, aluminum:3.8-4.4%, Ti:2.2-3.0%, C:0.05 - 0.09%, and B:0.008 to 0.03%.

[0008] The columnar crystal nickel radical heat-resistant alloy excellent in the intergranular corrosion-proof [elevated-temperature] nature of this invention is especially suitable as a raw material of a large-sized turbine blade. This invention Therefore, (3) Cr:12.0-14.3%, Co:8.5-11.0%, Mo: 1.0-3.5%, W:3.5 - 6.2%, Ta:3.0-5.5%, aluminum: 3.5-4.5%, Ti:2.0-3.2%, C:0.04 - 0.12%, B:0.005 to 0.05%, Zr:0.001-5ppm are contained and it has the description in the large-sized turbine blade excellent in the intergranular corrosion-proof [elevated-temperature] nature which has the presentation which the remainder becomes from nickel and an unescapable impurity made from a columnar crystal nickel radical heat-resistant-alloy casting.

[0009] The component presentation of nickel radical alloy which constitutes the large-sized turbine blade excellent in the intergranular corrosion-proof [elevated-temperature] nature of this invention made from a columnar crystal nickel radical heat-resistant-alloy casting By weight %, Cr:13-14%, Co:9.4-10.6%, Mo:1.2-2.0%, W:4.2 - 5.8%, Ta:4.0-5.2%, aluminum:3.8-4.4%, Ti: It is much more desirable to have the presentation which Zr:0.01-1ppm are contained and the remainder becomes from nickel and an unescapable impurity 2.2-3.0%, C:0.05 - 0.09%, and B:0.008 to 0.03%.

[0010] The columnar crystal nickel radical heat-resistant alloy excellent in the intergranular corrosion-proof [elevated-temperature] nature of this invention may contain Mg and/or calcium:1-100ppm, may contain 1 of Pt:0.02-0.5%, Rh:0.02-0.5%, and Re:0.02-0.5% of sorts, and two sorts or more further, and may contain these both sides.

[0011] This invention Therefore, (4) Cr:12.0-14.3%, Co:8.5-11.0%, Mo: 0.5-4%, W:3.5 - 6.2%, Ta:3.0-5.5%, aluminum: 3.5-4.5%, Ti:2.0-3.2%, C:0.04 - 0.12%, Zr:0.001-5ppm are contained B:0.005 to 0.05%.

The columnar crystal nickel radical heat-resistant-alloy large-sized casting excellent in the intergranular corrosion-proof [elevated-temperature] nature which has the presentation which Mg and/or calcium:1-100ppm are furthermore contained, and the remainder becomes from nickel and an unescapable impurity, (5) Cr:12.0-14.3%, Co:8.5-11.0%, Mo:0.5-4%, W:3.5 - 6.2%, Ta:3.0-5.5%, aluminum:3.5-4.5%, Ti: 2.0-3.2%, C:0.04 - 0.12%, B:0.005 - 0.05%, Zr:0.001-5ppm are contained. Further Pt:0.02-0.5%, 1 of Rh:0.02-0.5% and Re:0.02-0.5% of sorts and two sorts or more are contained. The columnar crystal nickel radical heat-resistant-alloy large-sized casting excellent in the intergranular corrosion-proof [elevated-temperature] nature which has the presentation which the remainder becomes from nickel and an unescapable impurity, (6) Cr:12.0-14.3%, Co:8.5-11.0%, Mo:0.5-4%, W:3.5 - 6.2%, Ta:3.0-5.5%, aluminum:3.5-4.5%, Ti: 2.0-3.2%, C:0.04 - 0.12%, B:0.005 - 0.05%, Contain Zr:0.001-5ppm and Mg and/or calcium:1-100ppm are contained further. Furthermore, 1 of Pt:0.02-0.5%, Rh:0.02-0.5%, and Re:0.02-0.5% of sorts and two sorts or more are contained. It has the description in the columnar crystal nickel radical heat-resistant-alloy large-sized casting excellent in the intergranular corrosion-proof [elevated-temperature] nature which has the presentation which the remainder becomes from nickel and an unescapable impurity.

[0012] The columnar crystal nickel radical heat-resistant alloy excellent in Mg of this invention and/or calcium, and the intergranular corrosion-proof [elevated-temperature] nature that contains one sort in Pt, Rh, and Re or two sorts or more further is especially suitable as a raw material of a large-sized turbine blade. This invention Therefore, (7) Cr:12.0-14.3%, Co:8.5-11.0%, Mo: 1.0-3.5%, W:3.5 - 6.2%, Ta:3.0-5.5%, aluminum: 3.5-4.5%, Ti:2.0-3.2%, C:0.04 - 0.12%, Zr:0.001-5ppm are contained B:0.005 to 0.05%. The large-sized turbine blade excellent in the intergranular corrosion-proof [elevated-temperature] nature which has the presentation which the remainder which has the presentation which Mg and/or calcium:1-100ppm are furthermore contained, and the remainder becomes from nickel and an unescapable impurity becomes from nickel and an unescapable impurity made from a columnar crystal nickel radical heat-resistant-alloy casting, (8) Cr:12.0-14.3%, Co:8.5-11.0%, Mo:1.0-3.5%, W:3.5 - 6.2%, Ta:3.0-5.5%, aluminum:3.5-4.5%, Ti: 2.0-3.2%, C:0.04 - 0.12%, B:0.005 - 0.05%, Zr:0.001-5ppm are contained. Further Pt:0.02-0.5%, 1 of Rh:0.02-0.5% and Re:0.02-0.5% of sorts and two sorts or more are contained. The large-sized turbine blade excellent in the intergranular corrosion-proof [elevated-temperature] nature which has the presentation which the remainder which has the presentation which the remainder becomes from nickel and an unescapable impurity becomes from nickel and an unescapable impurity made from a columnar crystal nickel radical heat-resistant-alloy casting, (9) Cr:12.0-14.3%, Co:8.5-11.0%, Mo:1.0-3.5%, W:3.5 - 6.2%, Ta:3.0-5.5%, aluminum:3.5-4.5%, Ti: 2.0-3.2%, C:0.04 - 0.12%, B:0.005 - 0.05%, Contain Zr:0.001-5ppm and Mg and/or calcium:1-100ppm are contained further. Furthermore, 1 of Pt:0.02-0.5%, Rh:0.02-0.5%, and Re:0.02-0.5% of sorts and two sorts or more are contained. It has the description in the large-sized turbine blade excellent in the intergranular corrosion-proof [elevated-temperature] nature which has the presentation which the remainder which has the presentation which the remainder becomes from nickel and an unescapable impurity becomes from nickel and an unescapable impurity made from a columnar crystal nickel radical heat-resistant-alloy casting.

[0013] Next, the reason for definition of an alloy presentation of the large-sized turbine blade made from a columnar crystal nickel radical heat-resistant-alloy casting excellent in a columnar crystal nickel radical heat-resistant-alloy large-sized casting and intergranular corrosion-proof [elevated-temperature] nature excellent in the intergranular corrosion-proof [elevated-temperature] nature of this invention is explained in full detail.

[0014] Cr industrial use gas turbine requires hot oxidation resistance and hot corrosion resistance, in order to contact the combustion gas containing the oxidizing quality and staining substance which were produced by combustion. Cr is an element which gives oxidation resistance and corrosion resistance to an alloy, and the effectiveness is so remarkable that the amount of Cr(s) in an alloy is made [many]. However, since Co, Mo, W, Ta, etc. are otherwise added with a columnar crystal nickel radical heat-resistant-alloy [which was excellent in the intergranular corrosion-proof / elevated-temperature / nature of this invention on the other hand] large-sized [amounts / at less than 12.0%, that effectiveness has few amounts of Cr(s), and] casting, in order to balance these, containing exceeding 14.3% is not desirable. Therefore, Cr content was defined to 12.0 - 14.3%. As mentioned above, as for Cr content contained in nickel radical heat-resistant alloy which produces the large-sized turbine blade excellent in the intergranular corrosion-proof [elevated-temperature] nature of this invention made from a columnar crystal nickel radical heat-resistant-alloy casting, it is much more desirable that it is 13 - 14%.

[0015] CoCo enlarges the limit (solid-solution limit) where Ti, aluminum, Ta, etc. are made to dissolve on a base at an elevated temperature. The amount of Co(es) needs to be 8.5% or more from a place with the

operation which raises the reinforcement of the columnar crystal nickel radical heat-resistant-alloy large-sized casting which was made to carry out the detailed distribution deposit of the gamma'phase (nickel3 (Ti, aluminum, Ta)), and was excellent in intergranular corrosion-proof [elevated-temperature] nature with heat treatment. On the other hand When Co content exceeded 11.0%, the balance with other elements, such as Cr, Mo, W, Ta, aluminum, and Ti, collapsed, and since the ductility lowering by the deposit of a harmful phase was brought about, Co content was defined to 8.5 - 11.0%. As for Co content contained in nickel radical heat-resistant alloy which produces the large-sized turbine blade excellent in the intergranular corrosion-proof [elevated-temperature] nature of this invention made from a columnar crystal nickel radical heat-resistant-alloy casting, it is much more desirable that it is 9.4 - 10.6%.

[0016] While there was an operation which it dissolves [operation] in a base and raises high temperature strength, there was effectiveness which contributes to high temperature strength by precipitation hardening, but less than 1.0% of MoMo was [the content] insufficient, and on the other hand, since it checked the ductility by the deposit of a harmful phase when it added too much exceeding 3.5%, it was defined to Mo:1.0-3.5%. As for Mo content contained in nickel radical heat-resistant alloy which produces the large-sized turbine blade excellent in the intergranular corrosion-proof [elevated-temperature] nature of this invention made from a columnar crystal nickel radical heat-resistant-alloy casting, it is much more desirable that it is 1.2 - 2.0%.

[0017] Although WW has an operation of solid solution strengthening and precipitation hardening like Mo and there is effectiveness which contributes to grant of high temperature strength If the amount is made [many / not much] too much required 3.5% or more, since it is an element with the large specific gravity of W itself while depositing a harmful phase, the specific gravity of the whole alloy will become large. In the turbine bucket which a centrifugal force commits, it was disadvantageous, and when casting the columnar crystal large-sized casting excellent in intergranular corrosion-proof [elevated-temperature] nature, a FUREKKURU defect came to occur, and the content was made into 3.5 - 6.2% from the place which becomes in cost and high further. As for W content contained in nickel radical heat-resistant alloy which produces the large-sized turbine blade excellent in the intergranular corrosion-proof [elevated-temperature] nature of this invention made from a columnar crystal nickel radical heat-resistant-alloy casting, it is much more desirable that it is 4.2 - 5.8%.

[0018] TiTi is an element required for the deposit of gamma'phase for raising the high temperature strength of a gamma'precipitation-hardening mold nickel radical alloy, and its less than 2.0% is [precipitation strengthening of gamma'phase] insufficient. Since a reaction with a variant will become intense and a casting surface will be worsened when casting the columnar crystal large-sized casting excellent in intergranular corrosion-proof [elevated-temperature] nature, while the amount of deposits increases too much and checking ductility if demand reinforcement cannot be satisfied and it adds too much so much more than 3.2%, it is not desirable. Therefore, Ti content was defined to 2.0 - 3.2%. As mentioned above, as for Ti content contained in nickel radical heat-resistant alloy which produces the large-sized turbine blade excellent in the intergranular corrosion-proof [elevated-temperature] nature of this invention made from a columnar crystal nickel radical heat-resistant-alloy casting, it is much more desirable that it is 2.2 - 3.0%.

[0019] While AlAl is the element which demonstrates the same effectiveness as Ti, generating gamma'phase and raising high temperature strength, it had the operation which contributes to the oxidation resistance in an elevated temperature, and corrosion-resistant grant, but the amount needed to be 3.5% or more, and on the other hand, if it adds too much in a large quantity not much exceeding 4.5%, in order to check ductility, aluminum content was defined to 3.5 - 4.5%. As for aluminum content contained in nickel radical heat-resistant alloy which produces the large-sized turbine blade excellent in the intergranular corrosion-proof [elevated-temperature] nature of this invention made from a columnar crystal nickel radical heat-resistant-alloy casting, it is much more desirable that it is 3.8 - 4.4%.

[0020] TaTa contributes to improvement in high temperature strength by solid solution strengthening and gamma'phase precipitation hardening, and is effective at 3.0% or more. On the other hand, since ductility was fallen when it added too much, it could be 5.5% or less. Therefore, although Ta content contained in nickel radical heat-resistant alloy which produces the large-sized turbine blade excellent in the intergranular corrosion-proof [elevated-temperature] nature of this invention made from a columnar crystal nickel radical heat-resistant-alloy casting was defined to 3.0 - 5.5%, it is much more desirable that it is 4.0 - 5.2%.

[0021] Since CC formed carbide, deposited especially on the grain boundary and a dendrite boundary, strengthened the grain boundary and the dendrite boundary and contributed to improvement in high temperature strength, it was required 0.04% or more, but since ductility was checked on the other hand when it added too much exceeding 0.12%, the content was made into 0.04 - 0.12%. The much more desirable

range of the content of C is 0.05 - 0.09%.
[0022] Since BB increases the bonding strength in the grain boundary, the grain boundary is strengthened and high temperature strength was raised, it was a required component, but the effectiveness of a request of the content at less than 0.005% was not acquired, but since there was a possibility of checking ductility when it adds on the other hand not much mostly, it could be 0.05% or less. The much more desirable range of the content of B is 0.008 - 0.03%.
[0023] Although ZrZr is required 0.001 ppm or more since it increases the corrosion resistance of the grain boundary and raises intergranular corrosion-proof [elevated-temperature] nature by carrying out minute amount addition Solution-heat-treatment temperature for detailed decentralization of a precipitation-strengthening phase cannot be raised from the place to which local melting temperature is reduced while Zr will segregate so much to the grain boundary and reducing the corrosion resistance of the grain boundary conversely, if it adds more mostly than 5 ppm. Since "divide" will occur if lowering of local melting temperature is disregarded, it raises to temperature required for detailed decentralization of a precipitation-strengthening phase and solution heat treatment is performed, it is not desirable. Therefore, the content of Zr was set to 0.001-5 ppm. The much more desirable range of the content of Zr is 0.01-1 ppm.
[0024] Mg from the place which will weaken association of the grain boundary on the contrary if operation sufficient in less than 1 ppm is not acquired although there is an operation which prevents Mg, CaMg, and/or calcium have strong bonding strength with impurities, such as oxygen and sulfur, and according to impurities, such as oxygen and sulfur, further ductility lowering, but contained exceeding 100 ppm on the other hand, and causes a crack, and/or calcium determined it as 1-100 ppm.
[0025] Although Pt, Rh, RePt, and Rh and Re have a corrosion-resistant improvement operation, since it is noble metals and a price becomes high, it is not desirable except that still much more effectiveness cannot be desired, if desired effectiveness is not acquired for the content at less than 0.02%, respectively but the content contains on the other hand exceeding 0.5%, respectively. Therefore, one sort in Pt, Rh, and Re or two sorts or more were defined to 0.02 - 0.5%, respectively.
[0026] In addition, although Hf is made into the indispensable constituent with the conventional columnar crystal nickel radical heat-resistant-alloy large-sized casting, it is not desirable to contain Hf with the columnar crystal nickel radical heat-resistant-alloy large-sized casting of this invention.
[0027] In order to manufacture the columnar crystal nickel radical heat-resistant-alloy large-sized casting excellent in the intergranular corrosion-proof [elevated-temperature] nature of this invention A columnar crystal nickel radical heat-resistant-alloy large-sized casting is produced by pulling down a chill plate at 1480-1530 degrees C, and reducing by rate:200 - 350 mm/h. one direction coagulation equipment -- mold stoving temperature whenever: -- 900 to 1600 atmospheric pressure and HIP of 1 - 5-hour maintenance are given to this at 1180-1265 degrees C. Solution heat treatment of maintenance is performed at 1200-1265 degrees C for 2 to 5 hours, and after holding at further 950-1080 degrees C for 2 to 10 hours, it is obtained by performing aging heat treatment of maintenance at 760-870 degrees C for 16 to 24 hours.
[0028]
[Embodiment of the Invention] Preparing nickel radical heat-resistant alloy which has the component presentation shown in a table 1 - a table 3, carrying out vacuum melting of this nickel radical heat-resistant alloy, respectively, and casting the molten metal of nickel radical heat-resistant alloy to the mold of one direction coagulation equipment Whenever [mold stoving temperature]: The columnar crystal large-sized cast plates 17-20 were produced this invention columnar crystal large-sized cast plates 1-16 and conventionally which pulls down 1600 degrees C and a chill plate and has a dimension (vertical:15mm, horizontal:100mm, and height:300mm) on condition that rate:120 mm/h.
[0029]
[A table 1]
this invention columnar crystal large-sized cast plate Element 1 2 3 4 5 6 7 8 Cr 13.1 14.0 12.5 13.5 13.3 12.2 13.3 14.2 Co 9.0 8.5 10.1 10.5 10.1 9.7 8.8 9.3 Mo 2.1 1.0 3.5 1.5 1.5 2.4 2.7 3.0 W 4.0 3.5 4.3 3.7 4.5 4.5 4.1 3.9 Ta 3.3 5.4 4.9 3.0 4.6 3.8 3.5 3.8 aluminum4.03.5 4.3 3.7 4.1 4.54.1 3.9Ti 2.72.3 3.2 2.5 2.72.9 3.02.8 C0.08 0.10 0.06 0.12 0.06 0.07 0.09 0.11B 0.011 0.009 0.007 0.0150.010 0.013 0.012 0.010Zr 1.32.6 1.24.3 0.05 0.005 0.1 0.6calcium - - - - - - 53 10 Mg - - - - - 81 - 12 Pt - - - - - - - - Rh - - - - - - - - Re - - - - - - - - nickel It remains. The remaining remainder It remains. It remains. It remains. The remaining remainder Weight %, however Zr, calcium and Mg are ppm. [0030]
[A table 2]
this invention columnar crystal large-sized cast plate Element 9 10 11 12 13 14 15 16 Cr 13.8 12.1 14.0 13.0 13.5 12.5 13.3 14.2 Co 9.5 9.0 8.5 10.1 10.5 9.7 8.8 9.3 Mo 1.8 2.1 1.1 3.5 1.5 2.4 2.7 3.0 W 4.2 4.0 3.5 4.3

3.8 4.6 4.1 3.9 Ta 4.5 3.3 5.3 4.9 3.1 3.8 3.5 3.8 aluminum 4.2 4.1 3.6 4.33.8 4.54.1 3.9Ti 2.7 2.7 2.2 3.12.5 2.93.0 2.8 C 0.08 0.08 0.10 0.07 0.12 0.07 0.090.11 B 0.0050.011 0.039 0.007 0.015 0.013 0.0120.010 Zr 19 0.30.8 1.92.3 3.60.03 0.7 calcium 18 - - - 25 74 34 10 Mg 72 - - - 37 5 54 12 Pt - 0.05 0.1- 0.2 0.06 0.2 0.05 Rh - 0.05 0.2 0.1 0.1 - - 0.05 Re - 0.05 - 0.3 - 0.07 0.1 0.05 nickel remainder It remains. It remains. It remains. It remains. The remaining remainder It remains. Weight %, however Zr, calcium and Mg are ppm.

[0031]

[A table 3]

従来柱状晶大型大型鋳物板

元素	18	19	20	21
Cr	14.1	13.8	13.9	14.2
Co	9.9	10.2	10.3	9.6
Mo	1.5	1.6	1.6	1.4
W	4.3	4.4	4.3	4.1
Ta	4.6	4.8	4.8	4.6
Al	4.1	4.1	4.0	3.9
Ti	2.8	2.6	2.7	2.7
C	0.08	0.09	0.08	0.10
B	0.014	0.011	0.009	0.013
Zr	0.037	0.022	0.013	0.023
Hf	−	−	1.5	0.7
Ca	−	12	−	28
Mg	31	5	80	29
Pt	−	−	−	−
Rh	−	−	−	−
Re	−	−	−	−
Ni	残り	残り	残り	残り

重量%（Ｚｒも含む）、
ただし、ＣａおよびＭｇはｐｐｍ

[0032] The columnar crystal large-sized cast plates 17-20 the obtained this invention columnar crystal large-sized cast plates 1-16 and conventionally The inside of Ar ambient atmosphere, Temperature : HIP of the conditions of maintenance is given to 1180 degrees C and 1500 atmospheric pressures for 2 hours. Subsequently, inside of a vacuum ambient atmosphere, temperature : After making it 1240 degrees C at the time of 2-hour maintenance, solution treatment of the conditions of cooling is performed by Ar gas fan. Then, inside of a vacuum ambient atmosphere, temperature: After making it 1050 degrees C at the time of 5-hour maintenance, it cooled by Ar gas fan, and succeedingly, among a vacuum ambient atmosphere and after making it temperature:870 degree C at the time of 18-hour maintenance, the 2nd-step aging treatment of the conditions of cooling was performed by Ar gas fan.

[0033] The columnar crystal large-sized cast plates 17-20 are cut down by machining this invention columnar crystal large-sized cast plates 1-16 and conventionally which performed said HIP and heat treatment. Diameter:10mm, Die length : Produce a test piece with a dimension of 20mm and the obtained test piece is immersed in temperature:950 degree C fused salt (Na[20wt% and NaCl:5wt% and]2 CO3 : Na2 SO4 : 75wt%). It cooled, after holding for 150 hours in the electric furnace which took out after that and was held at 900 degrees C. This test piece was cut, and it gazed at the microstructure of a cross section by SEM (scanning electron microscope), and asked for the average pervasion depth which advanced along the grain boundary, that result was shown in a table 4, and intergranular corrosion-proof [elevated-temperature] nature was evaluated.

[0034]

[A table 4]

種 別		平均侵食深さ（μm）	種 別		平均侵食深さ（μm）
本発明柱状晶大型鋳物板	1	34	本発明柱状晶大型鋳物板	11	47
	2	88		12	151
	3	84		13	124
	4	167		14	175
	5	48		15	91
	6	105		16	59
	7	62	従来柱状晶大型鋳物板	17	701
	8	57		18	560
	9	70		19	498
	10	188		20	545

[0035]
[Effect of the Invention] The result shown in a table 1 - a table 4 shows that this invention columnar crystal large-sized [from the place where the average pervasion depth is small] cast plates 1-16 are excellent in intergranular corrosion-proof [elevated-temperature] nature compared with the columnar crystal large-sized cast plates 17-20 conventionally in which this invention columnar crystal large-sized cast plates 1-16 contain many Zr. Therefore, from a place excellent in intergranular corrosion-proof [elevated-temperature] nature, even if it uses the columnar crystal nickel radical heat-resistant-alloy large-sized casting of this invention under a severe condition as turbine ** and **** of a gas turbine, and a bucket of an elevated-temperature blower, it can be used for a long period of time, continuing, and it does so the effectiveness which was excellent on industry.

[Translation done.]

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最終頁に続く

(54)【発明の名称】　高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金大型鋳物

(57)【特許請求の範囲】
【請求項１】　重量%で、Ｃｒ：１２．０～１４．３%、Ｃｏ：８．５～１１．０%、Ｍｏ：１．０～３．５%、Ｗ：３．５～６．２%、Ｔａ：３．０～５．５%、Ａｌ：３．５～４．５%、Ｔｉ：２．０～３．２%、Ｃ：０．０４～０．１２%、Ｂ：０．００５～０．０５%、Ｚｒ：０．００１～５ｐｐｍを含有し、残部がＮｉおよび不可避不純物からなる組成を有することを特徴とする高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金大型鋳物。
【請求項２】　重量%で、Ｃｒ：１２．０～１４．３%、Ｃｏ：８．５～１１．０%、Ｍｏ：１．０～３．５%、Ｗ：３．５～６．２%、Ｔａ：３．０～５．５%、Ａｌ：３．５～４．５%、Ｔｉ：２．０～３．２%、Ｃ：０．０４～０．１２%、Ｂ：０．００５～０．０５%、Ｚｒ：０．００１～５ｐｐｍを含有し、さらにＭｇおよび／またはＣａ：０．５～１００ｐｐｍを含有し、残部がＮｉおよび不可避不純物からなる組成を有することを特徴とする高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金大型鋳物。
【請求項３】　重量%で、Ｃｒ：１２．０～１４．３%、Ｃｏ：８．５～１１．０%、Ｍｏ：１．０～３．５%、Ｗ：３．５～６．２%、Ｔａ：３．０～５．５%、Ａｌ：３．５～４．５%、Ｔｉ：２．０～３．２%、Ｃ：０．０４～０．１２%、Ｂ：０．００５～０．０５%、Ｚｒ：０．００１～５ｐｐｍを含有し、さらにＰｔ：０．０２～０．５%、Ｒｈ：０．０２～０．５%、Ｒｅ：０．０２～０．５%の内の１種または２種以上を含有し、残部がＮｉおよび不可避不純物からなる組成を有することを特徴とする高温耐粒界腐食性に

優れた柱状晶Ｎｉ基耐熱合金大型鋳物。

【請求項４】　重量%で、Ｃｒ：１２．０～１４．３%、Ｃｏ：８．５～１１．０%、Ｍｏ：１．０～３．５%、Ｗ：３．５～６．２%、Ｔａ：３．０～５．５%、Ａｌ：３．５～４．５%、Ｔｉ：２．０～３．２%、Ｃ：０．０４～０．１２%、Ｂ：０．００５～０．０５%、Ｚｒ：０．００１～５ｐｐｍを含有し、さらにＭｇおよび／またはＣａ：０．５～１００ｐｐｍを含有し、さらにＰｔ：０．０２～０．５%、Ｒｈ：０．０２～０．５%、Ｒｅ：０．０２～０．５%の内の１種または２種以上を含有し、残部がＮｉおよび不可避不純物からなる組成を有することを特徴とする高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金大型鋳物。

【請求項５】　請求項１、２、３または４記載の高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金鋳物からなることを特徴とする大型タービン翼。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】この発明は、高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金大型鋳物に関するものであり、特に高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金鋳物で構成されたガスタービンのタービン動・静翼および高温ブロアーの動翼として使用される大型タービン翼に関するものである。

【０００２】

【従来の技術】ガスタービンのタービン動・静翼、高温ブロアーの動翼はＮｉ基耐熱合金鋳物で構成されることは知られているところであり、例えば、特開平６－５７３９５号公報には、ガスタービンのタービン動・静翼、高温ブロアーの動翼を作るためのＮｉ基耐熱合金として、重量%（以下、%は、重量%を示す）で、（ａ）Ｃｒ：１３．１～１５．０%、Ｃｏ：８．５～１０．５%、Ｍｏ：１．０～３．５%、Ｗ：３．５～４．５%、Ｔａ：３．０～５．５%、Ａｌ：３．５～４．５%、Ｔｉ：２．０～３．２%、Ｃ：０．０６～０．１２%、Ｂ：０．００５～０．０２５%、Ｚｒ：０．０１０～０．０５０%、Ｍｇおよび／またはＣａ：１～１００ｐｐｍを含有し、残部がＮｉおよび不可避不純物からなる組成を有する、高温強度、高温耐酸化性および高温耐蝕性に優れたＮｉ基耐熱合金、（ｂ）Ｃｒ：１３．１～１５．０%、Ｃｏ：８．５～１０．５%、Ｍｏ：１．０～３．５%、Ｗ：３．５～４．５%、Ｔａ：３．０～５．５%、Ａｌ：３．５～４．５%、Ｔｉ：２．０～３．２%、Ｃ：０．０６～０．１２%、Ｂ：０．００５～０．０２５%、Ｚｒ：０．０１０～０．０５０%、さらに、Ｈｆ：０．２～１．５%を含有し、Ｍｇおよび／またはＣａ：１～１００ｐｐｍを含有し、残部がＮｉおよび不可避不純物からなる組成を有する、高温強度、高温耐酸化性および高温耐蝕性に優れたＮｉ基耐熱合金、（ｃ）

Ｃｒ：１３．１～１５．０%、Ｃｏ：８．５～１０．５%、Ｍｏ：１．０～３．５%、Ｗ：３．５～４．５%、Ｔａ：３．０～５．５%、Ａｌ：３．５～４．５%、Ｔｉ：２．０～３．２%、Ｃ：０．０６～０．１２%、Ｂ：０．００５～０．０２５%、Ｚｒ：０．０１０～０．０５０%、Ｍｇおよび／またはＣａ：１～１００ｐｐｍを含有し、さらに、Ｈｆ：０．２～１．５%を含有し、さらに、Ｐｔ：０．０２～０．５%、Ｒｈ：０．０２～０．５%、Ｒｅ：０．０２～０．５%の内の１種または２種以上を含有し、残部がＮｉおよび不可避不純物からなる組成を有する、高温強度、高温耐酸化性および高温耐蝕性に優れたＮｉ基耐熱合金、（ｄ）Ｃｒ：１３．１～１５．０%、Ｃｏ：８．５～１０．５%、Ｍｏ：１．０～３．５%、Ｗ：３．５～４．５%、Ｔａ：３．０～５．５%、Ａｌ：３．５～４．５%、Ｔｉ：２．０～３．２%、Ｃ：０．０６～０．１２%、Ｂ：０．００５～０．０２５%、Ｚｒ：０．０１０～０．０５０%、Ｍｇおよび／またはＣａ：１～１００ｐｐｍを含有し、さらにＨｆ：０．２～１．５%を含有し、さらにＰｔ：０．０２～０．５%、Ｒｈ：０．０２～０．５%、Ｒｅ：０．０２～０．５%の内の１種または２種以上を含有し、残部がＮｉおよび不可避不純物からなる組成を有する、高温強度、高温耐酸化性および高温耐蝕性に優れたＮｉ基耐熱合金、などが記載されている。

【０００３】一方、ガスタービンのタービン動・静翼および高温ブロアーの動翼は柱状晶Ｎｉ基耐熱合金鋳物で構成されることも知られている。この柱状晶Ｎｉ基耐熱合金鋳物を製造するには、通常の一方向凝固装置を使用する。この一方向凝固装置において、真空チャンバー内を真空引きし、溶解炉で溶解されたＮｉ基合金溶湯を、チル板上に固定しかつ１４８０～１５３０℃の温度に加熱した鋳型に注入したのち、鋳型を水冷チルリングを通してチル板を引き下げ速度：２００～３５０ｍｍ／ｈで下方に引き下げ、チル板に形成された柱状晶を成長させることにより長尺の柱状晶Ｎｉ基耐熱合金鋳物を製造する。

【０００４】

【発明が解決しようとする課題】近年、ガスタービンの大型化に伴って、そこに据え付けられるタービン翼も大型化している。しかし、従来のＮｉ基耐熱合金で柱状晶Ｎｉ基耐熱合金鋳物、特に柱状晶Ｎｉ基耐熱合金鋳物からなる大型のタービン翼を製造すると、結晶粒が粗大化し、合金成分の偏析が大きくなって成分偏析の最も大きい結晶粒界では粒界腐食が著しく進行するところから、高温耐粒界腐食性が大幅に低下し、柱状晶Ｎｉ基耐熱合金鋳物からなる大型タービン翼の信頼性と寿命が低下していた。

【０００５】

【課題を解決する手段】そこで本発明者等は大型タービン翼の高温耐粒界腐食性を向上させるべく鋭意研究した

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結果、Ｎｉ基合金に添加するＺｒ量を極微量に制限して、Ｃｒ：１２．０～１４．３％、Ｃｏ：８．５～１１．０％、Ｍｏ：１．０～３．５％、Ｗ：３．５～６．２％、Ｔａ：３．０～５．５％、Ａｌ：３．５～４．５％、Ｔｉ：２．０～３．２％、Ｃ：０．０４～０．１２％、Ｂ：０．００５～０．０５％、Ｚｒ：０．００１～５ｐｐｍを含有し、残部がＮｉおよび不可避不純物からなる組成に限定し、かかる組成のＮｉ基合金を溶解して得られた溶湯を一方向凝固装置の鋳型に注入しながらチル板を引き下げ、得られた柱状晶Ｎｉ基耐熱合金鋳物を１１８０～１２６５℃で９００～１６００気圧、１～５時間保持のＨＩＰを施し、従来よりも高温の１２００～１２６５℃で２～５時間保持の溶体化熱処理を施し、さらに９５０～１０８０℃で２～１０時間保持したのち７６０～８７０℃で１６～２４時間保持の時効熱処理を施すと、従来よりも高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金鋳物が得られ、この高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金鋳物からなる大型のタービン翼は従来よりも高温耐粒界腐食性に優れた特性を有することを知見し、この発明に至ったのである。

【０００６】この発明は、かかる知見に基づいてなされたものであって、（１）Ｃｒ：１２．０～１４．３％、Ｃｏ：８．５～１１．０％、Ｍｏ：０．５～４％、Ｗ：３．５～６．２％、Ｔａ：３．０～５．５％、Ａｌ：３．５～４．５％、Ｔｉ：２．０～３．２％、Ｃ：０．０４～０．１２％、Ｂ：０．００５～０．０５％、Ｚｒ：０．００１～５ｐｐｍを含有し、残部がＮｉおよび不可避不純物からなる組成を有する高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金大型鋳物、に特徴を有するものである。

【０００７】この発明の高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金大型鋳物を構成するＮｉ基合金の成分組成は、重量％で、Ｃｒ：１３～１４％、Ｃｏ：９．４～１０．６％、Ｍｏ：１．２～２．０％、Ｗ：４．２～５．８％、Ｔａ：４．０～５．２％、Ａｌ：３．８～４．４％、Ｔｉ：２．２～３．０％、Ｃ：０．０５～０．０９％、Ｂ：０．００８～０．０３％、Ｚｒ：０．０１～１ｐｐｍを含有し、残部がＮｉおよび不可避不純物からなることが一層好ましい。

【０００８】この発明の高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金は特に大型のタービン翼の素材として適している。従って、この発明は、（３）Ｃｒ：１２．０～１４．３％、Ｃｏ：８．５～１１．０％、Ｍｏ：１．０～３．５％、Ｗ：３．５～６．２％、Ｔａ：３．０～５．５％、Ａｌ：３．５～４．５％、Ｔｉ：２．０～３．２％、Ｃ：０．０４～０．１２％、Ｂ：０．００５～０．０５％、Ｚｒ：０．００１～５ｐｐｍを含有し、残部がＮｉおよび不可避不純物からなる組成を有する高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金鋳物製大型タービン翼、に特徴を有するものである。

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【０００９】この発明の高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金鋳物製大型タービン翼を構成するＮｉ基合金の成分組成は、重量％で、Ｃｒ：１３～１４％、Ｃｏ：９．４～１０．６％、Ｍｏ：１．２～２．０％、Ｗ：４．２～５．８％、Ｔａ：４．０～５．２％、Ａｌ：３．８～４．４％、Ｔｉ：２．２～３．０％、Ｃ：０．０５～０．０９％、Ｂ：０．００８～０．０３％、Ｚｒ：０．０１～１ｐｐｍを含有し、残部がＮｉおよび不可避不純物からなる組成を有することが一層好ましい。

【００１０】この発明の高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金は、Ｍｇおよび／またはＣａ：１～１００ｐｐｍを含有してもよく、さらにＰｔ：０．０２～０．５％、Ｒｈ：０．０２～０．５％、Ｒｅ：０．０２～０．５％の内の１種または２種以上を含有してもよく、これら双方を含有してもよい。

【００１１】従って、この発明は、（４）Ｃｒ：１２．０～１４．３％、Ｃｏ：８．５～１１．０％、Ｍｏ：０．５～４％、Ｗ：３．５～６．２％、Ｔａ：３．０～５．５％、Ａｌ：３．５～４．５％、Ｔｉ：２．０～３．２％、Ｃ：０．０４～０．１２％、Ｂ：０．００５～０．０５％、Ｚｒ：０．００１～５ｐｐｍを含有し、さらにＭｇおよび／またはＣａ：１～１００ｐｐｍを含有し、残部がＮｉおよび不可避不純物からなる組成を有する高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金大型鋳物、（５）Ｃｒ：１２．０～１４．３％、Ｃｏ：８．５～１１．０％、Ｍｏ：０．５～４％、Ｗ：３．５～６．２％、Ｔａ：３．０～５．５％、Ａｌ：３．５～４．５％、Ｔｉ：２．０～３．２％、Ｃ：０．０４～０．１２％、Ｂ：０．００５～０．０５％、Ｚｒ：０．００１～５ｐｐｍを含有し、さらにＰｔ：０．０２～０．５％、Ｒｈ：０．０２～０．５％、Ｒｅ：０．０２～０．５％の内の１種または２種以上を含有し、残部がＮｉおよび不可避不純物からなる組成を有する高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金大型鋳物、（６）Ｃｒ：１２．０～１４．３％、Ｃｏ：８．５～１１．０％、Ｍｏ：０．５～４％、Ｗ：３．５～６．２％、Ｔａ：３．０～５．５％、Ａｌ：３．５～４．５％、Ｔｉ：２．０～３．２％、Ｃ：０．０４～０．１２％、Ｂ：０．００５～０．０５％、Ｚｒ：０．００１～５ｐｐｍを含有し、さらにＭｇおよび／またはＣａ：１～１００ｐｐｍを含有し、さらにＰｔ：０．０２～０．５％、Ｒｈ：０．０２～０．５％、Ｒｅ：０．０２～０．５％の内の１種または２種以上を含有し、残部がＮｉおよび不可避不純物からなる組成を有する高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金大型鋳物、に特徴を有するものである。

【００１２】この発明のＭｇおよび／またはＣａ、さらにＰｔ、Ｒｈ、Ｒｅの内の１種または２種以上を含有する高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金は特

に大型のタービン翼の素材として適している。従って、この発明は、（７）Ｃｒ：１２．０～１４．３%、Ｃｏ：８．５～１１．０%、Ｍｏ：１．０～３．５%、Ｗ：３．５～６．２%、Ｔａ：３．０～５．５%、Ａｌ：３．５～４．５%、Ｔｉ：２．０～３．２%、Ｃ：０．０４～０．１２%、Ｂ：０．００５～０．０５%、Ｚｒ：０．００１～５ｐｐｍを含有し、さらにＭｇおよび／またはＣａ：１～１００ｐｐｍを含有し、残部がＮｉおよび不可避不純物からなる組成を有する残部がＮｉおよび不可避不純物からなる組成を有する高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金鋳物製大型タービン翼、（８）Ｃｒ：１２．０～１４．３%、Ｃｏ：８．５～１１．０%、Ｍｏ：１．０～３．５%、Ｗ：３．５～６．２%、Ｔａ：３．０～５．５%、Ａｌ：３．５～４．５%、Ｔｉ：２．０～３．２%、Ｃ：０．０４～０．１２%、Ｂ：０．００５～０．０５%、Ｚｒ：０．００１～５ｐｐｍを含有し、さらにＰｔ：０．０２～０．５%、Ｒｈ：０．０２～０．５%、Ｒｅ：０．０２～０．５%の内の１種または２種以上を含有し、残部がＮｉおよび不可避不純物からなる組成を有する残部がＮｉおよび不可避不純物からなる組成を有する高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金鋳物製大型タービン翼、（９）Ｃｒ：１２．０～１４．３%、Ｃｏ：８．５～１１．０%、Ｍｏ：１．０～３．５%、Ｗ：３．５～６．２%、Ｔａ：３．０～５．５%、Ａｌ：３．５～４．５%、Ｔｉ：２．０～３．２%、Ｃ：０．０４～０．１２%、Ｂ：０．００５～０．０５%、Ｚｒ：０．００１～５ｐｐｍを含有し、さらにＭｇおよび／またはＣａ：１～１００ｐｐｍを含有し、さらにＰｔ：０．０２～０．５%、Ｒｈ：０．０２～０．５%、Ｒｅ：０．０２～０．５%の内の１種または２種以上を含有し、残部がＮｉおよび不可避不純物からなる組成を有する残部がＮｉおよび不可避不純物からなる組成を有する高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金鋳物製大型タービン翼、に特徴を有するものである。

【００１３】次に、この発明の高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金大型鋳物および高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金鋳物製大型タービン翼の合金組成の限定理由について詳述する。

【００１４】Ｃｒ

産業用ガスタービンでは、燃焼によって生じた酸化性および腐食性物質を含有する燃焼ガスと接触するため、高温における耐酸化性及び耐蝕性が要求される。Ｃｒは合金に耐酸化性、耐蝕性を付与する元素であり、合金中におけるＣｒ量を多くする程、その効果は顕著である。しかし、Ｃｒ量が１２．０%未満ではその効果は少なく、一方、この発明の高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金大型鋳物では、他にＣｏ、Ｍｏ、Ｗ、Ｔａ等も添加されるため、これらとのバランスをとるため１４．３%を越えて含有することは好ましくない。よって、Ｃｒ含有量は１２．０～１４．３%に定めた。上述のように、この発明の高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金鋳物製大型タービン翼を作製するＮｉ基耐熱合金に含まれるＣｒ含有量は１３～１４%であることが一層好ましい。

【００１５】Ｃｏ

Ｃｏは、Ｔｉ、Ａｌ、Ｔａ等を高温で素地に固溶させる限度（固溶限）を大きくさせ、熱処理によってγ´相（Ni_3（Ｔｉ，Ａｌ，Ｔａ））を微細分散析出させて高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金大型鋳物の強度を向上させる作用があるところからＣｏ量は８．５%以上であることが必要であり、一方、Ｃｏ含有量が１１．０%を越えると、Ｃｒ、Ｍｏ、Ｗ、Ｔａ、Ａｌ、Ｔｉ等の他の元素とのバランスが崩れ、有害相の析出による延性低下をもたらすことからＣｏ含有量は８．５～１１．０%に定めた。この発明の高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金鋳物製大型タービン翼を作製するＮｉ基耐熱合金に含まれるＣｏ含有量は９．４～１０．６%であることが一層好ましい。

【００１６】Ｍｏ

Ｍｏは、素地中に固溶して、高温強度を上昇させる作用があると同時に、析出硬化によって高温強度に寄与する効果があるが、その含有量が、１．０%未満では不十分であり、一方、３．５%を越えて添加し過ぎると有害相の析出による延性を阻害するのでＭｏ：１．０～３．５%に定めた。この発明の高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金鋳物製大型タービン翼を作製するＮｉ基耐熱合金に含まれるＭｏ含有量は１．２～２．０%であることが一層好ましい。

【００１７】Ｗ

ＷはＭｏと同様に固溶強化と析出硬化の作用があり、高温強度の付与に寄与する効果があるが、その量は３．５%以上必要であり、また、あまり多くし過ぎると、有害相を析出するとともにＷ自身比重が大きい元素であるため合金全体の比重が大きくなり、遠心力の働くタービン動翼では不利であり、高温耐粒界腐食性に優れた柱状晶大型鋳物を鋳造するときにフレックル欠陥が発生するようになり、さらにコスト的にも高くなるところから、その含有量は、３．５～６．２%とした。この発明の高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金鋳物製大型タービン翼を作製するＮｉ基耐熱合金に含まれるＷ含有量は４．２～５．８%であることが一層好ましい。

【００１８】Ｔｉ

Ｔｉはγ´析出硬化型Ni基合金の高温強度を上げるためのγ´相の析出に必要な元素であり、２．０%未満ではγ´相の析出強化が不十分で、要求強度を満足することができず、また、３．２%よりも多量に添加し過ぎると析出量が多くなり過ぎて延性を阻害するとともに、高温耐粒界腐食性に優れた柱状晶大型鋳物を鋳造するときに異型との反応が激しくなり、鋳肌を悪くするので好まし

くない。従って、Ｔｉ含有量は２．０～３．２%に定めた。上述のように、この発明の高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金鋳物製大型タービン翼を作製するＮｉ基耐熱合金に含まれるＴｉ含有量は２．２～３．０%であることが一層好ましい。

【００１９】Ａｌ

ＡｌはＴｉと同様の効果を発揮する元素で、γ´相を生成し、高温強度を上げると共に、高温での耐酸化性、耐蝕性の付与に寄与する作用を有するが、その量は３．５%以上であることが必要であり、一方、４．５%を越えてあまり多量に添加し過ぎると延性を阻害するためにＡｌ含有量は３．５～４．５%に定めた。この発明の高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金鋳物製大型タービン翼を作製するＮｉ基耐熱合金に含まれるＡｌ含有量は３．８～４．４%であることが一層好ましい。

【００２０】Ｔａ

Ｔａは固溶強化及びγ´相析出硬化により高温強度の向上に寄与し、３．０%以上で効果がある。一方、添加し過ぎると延性を低下するので５．５%以下とした。従って、この発明の高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金鋳物製大型タービン翼を作製するＮｉ基耐熱合金に含まれるＴａ含有量は３．０～５．５%に定めたが、４．０～５．２%であることが一層好ましい。

【００２１】Ｃ

Ｃは炭化物を形成し、特に結晶粒界、樹枝状晶境界に析出して粒界や樹枝状晶境界を強化し、高温強度の向上に寄与するので０．０４%以上必要であるが、一方、０．１２%を越えて添加し過ぎると延性を阻害するのでその含有量を０．０４～０．１２%とした。Ｃの含有量の一層好ましい範囲は０．０５～０．０９%である。

【００２２】Ｂ

Ｂは結晶粒界における結合力を増して結晶粒界を強化し、高温強度を上昇させるので必要な成分であるが、その含有量が０．００５%未満では所望の効果が得られず、一方、あまり多く添加すると延性を阻害する恐れがあるため０．０５%以下とした。Ｂの含有量の一層好ましい範囲は０．００８～０．０３%である。

【００２３】Ｚｒ

Ｚｒは微量添加することにより結晶粒界の耐食性を増して高温耐粒界腐食性を上昇させるので０．００１ｐｐｍ以上必要であるが、５ｐｐｍよりも多く添加すると、結晶粒界にＺｒが多量に偏析して逆に結晶粒界の耐食性を低下させると共に局部的な溶融温度を低下させるところから析出強化相の微細分散化のための溶体化熱処理温度を上げることができず、局部的な溶融温度の低下を無視して析出強化相の微細分散化に必要な温度まで上げて溶＊

＊体化熱処理を行うと「割れ」が発生するので好ましくない。したがって、Ｚｒの含有量は０．００１～５ｐｐｍに定めた。Ｚｒの含有量の一層好ましい範囲は０．０１～１ｐｐｍである。

【００２４】ＭｇおよびまたはＣａ

ＭｇおよびまたはＣａは酸素、硫黄等の不純物との結合力が強く、さらに酸素、硫黄等の不純物による延性低下を防止する作用があるが、１ｐｐｍ未満では十分な作用が得られず、一方、１００ｐｐｍを越えて含有するとかえって結晶粒界の結合を弱めて割れの原因になるところからＭｇおよびまたはＣａは１～１００ｐｐｍと定めた。

【００２５】Ｐｔ、Ｒｈ、Ｒｅ

Ｐｔ、Ｒｈ、Ｒｅは耐食性向上作用があるが、その含有量がそれぞれ０．０２%未満では所望の効果が得られず、一方、その含有量がそれぞれ０．５%を越えて含有すると、なお一層の効果が望めないほか、貴金属であるために価格が高くなるので好ましくない。したがって、Ｐｔ、Ｒｈ、Ｒｅの内の１種または２種以上はそれぞれ０．０２～０．５%に定めた。

【００２６】その他

従来の柱状晶Ｎｉ基耐熱合金大型鋳物ではＨｆを必須構成成分としているが、この発明の柱状晶Ｎｉ基耐熱合金大型鋳物ではＨｆを含有することは好ましくない。

【００２７】この発明の高温耐粒界腐食性に優れた柱状晶Ｎｉ基耐熱合金大型鋳物を製造するには、一方向凝固装置により鋳型加熱温度：１４８０～１５３０℃でチル板を引き下げ速度：２００～３５０ｍｍ／ｈで引き下げることにより柱状晶Ｎｉ基耐熱合金大型鋳物を作製し、これに１１８０～１２６５℃で９００～１６００気圧、１～５時間保持のＨＩＰを施し、１２００～１２６５℃で２～５時間保持の溶体化熱処理を施し、さらに９５０～１０８０℃で２～１０時間保持したのち７６０～８７０℃で１６～２４時間保持の時効熱処理を施すことにより得られる。

【００２８】

【発明の実施の形態】表１～表３に示される成分組成を有するＮｉ基耐熱合金を用意し、このＮｉ基耐熱合金をそれぞれ真空溶解し、Ｎｉ基耐熱合金の溶湯を一方向凝固装置の鋳型に鋳込みながら、鋳型加熱温度：１６００℃、チル板を引き下げ速度：１２０ｍｍ／ｈの条件で、縦：１５ｍｍ、横：１００ｍｍ、高さ：３００ｍｍの寸法を有する本発明柱状晶大型鋳物板１～１６および従来柱状晶大型鋳物板１７～２０を作製した。

【００２９】

【表１】

本発明柱状晶大型鋳物板

元素	1	2	3	4	5	6	7	8
Ｃｒ	13.1	14.0	12.5	13.5	13.3	12.2	13.3	14.2
Ｃｏ	9.0	8.5	10.1	10.5	10.1	9.7	8.8	9.3

	11							12
Mo	2.1	1.0	3.5	1.5	1.5	2.4	2.7	3.0
W	4.0	3.5	4.3	3.7	4.5	4.5	4.1	3.9
Ta	3.3	5.4	4.9	3.0	4.6	3.8	3.5	3.8
Al	4.0	3.5	4.3	3.7	4.1	4.5	4.1	3.9
Ti	2.7	2.3	3.2	2.5	2.7	2.9	3.0	2.8
C	0.08	0.10	0.06	0.12	0.06	0.07	0.09	0.11
B	0.011	0.009	0.007	0.015	0.010	0.013	0.012	0.010
Zr	1.3	2.6	1.2	4.3	0.05	0.005	0.1	0.6
Ca	−	−	−	−	−	−	53	10
Mg	−	−	−	−	−	81	−	12
Pt	−	−	−	−	−	−	−	−
Rh	−	−	−	−	−	−	−	−
Re	−	−	−	−	−	−	−	−
Ni	残り	残り	残り	残り	残り	残り	残り	残り

重量%、ただし、Ｚｒ、ＣａおよびＭｇはｐｐｍ

【００３０】

＊ ＊【表２】

本発明柱状晶大型鋳物板

元素	9	10	11	12	13	14	15	16
Cr	13.8	12.1	14.0	13.0	13.5	12.5	13.3	14.2
Co	9.5	9.0	8.5	10.1	10.5	9.7	8.8	9.3
Mo	1.8	2.1	1.1	3.5	1.5	2.4	2.7	3.0
W	4.2	4.0	3.5	4.3	3.8	4.6	4.1	3.9
Ta	4.5	3.3	5.3	4.9	3.1	3.8	3.5	3.8
Al	4.2	4.1	3.6	4.3	3.8	4.5	4.1	3.9
Ti	2.7	2.7	2.2	3.1	2.5	2.9	3.0	2.8
C	0.08	0.08	0.10	0.07	0.12	0.07	0.09	0.11
B	0.005	0.011	0.039	0.007	0.015	0.013	0.012	0.010
Zr	19	0.3	0.8	1.9	2.3	3.6	0.03	0.7
Ca	18	−	−	−	25	74	34	10
Mg	72	−	−	−	37	5	54	12
Pt	−	0.05	0.1	−	0.2	0.06	0.2	0.05
Rh	−	0.05	0.2	0.1	0.1	−	−	0.05
Re	−	0.05	−	0.3	−	0.07	0.1	0.05
Ni	残り	残り	残り	残り	残り	残り	残り	残り

重量%、ただし、Ｚｒ、ＣａおよびＭｇはｐｐｍ

【００３１】

【表３】

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従来柱状晶大型大型鋳物板

元素	18	19	20	21
Ｃｒ	14.1	13.8	13.9	14.2
Ｃｏ	9.9	10.2	10.3	9.6
Ｍｏ	1.5	1.6	1.6	1.4
Ｗ	4.3	4.4	4.3	4.1
Ｔａ	4.6	4.8	4.8	4.6
Ａｌ	4.1	4.1	4.0	3.9
Ｔｉ	2.8	2.6	2.7	2.7
Ｃ	0.08	0.09	0.08	0.10
Ｂ	0.014	0.011	0.009	0.013
Ｚｒ	0.037	0.022	0.013	0.023
Ｈｆ	－	－	1.5	0.7
Ｃａ	－	12	－	28
Ｍｇ	31	5	80	29
Ｐｔ	－	－	－	－
Ｒｈ	－	－	－	－
Ｒｅ	－	－	－	－
Ｎｉ	残り	残り	残り	残り

重量％（Ｚｒも含む）、
ただし、ＣａおよびＭｇはｐｐｍ

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＊および従来柱状晶大型鋳物板１７～２０をＡｒ雰囲気中、温度：１１８０℃、１５００気圧に２時間保持の条件のＨＩＰを施し、ついで真空雰囲気中、温度：１２４０℃に２時間保持時した後Ａｒガスファンで冷却の条件の溶体化処理を施し、その後、真空雰囲気中、温度：１０５０℃に５時間保持時した後Ａｒガスファンで冷却し、引き続いて真空雰囲気中、温度：８７０℃に１８時間保持時した後Ａｒガスファンで冷却の条件の第２段時効処理を施した。

【００３３】前記ＨＩＰおよび熱処理を施した本発明柱状晶大型鋳物板１～１６および従来柱状晶大型鋳物板１７～２０を機械加工により切り出して直径：１０ｍｍ、長さ：２０ｍｍの寸法の試験片を作製し、得られた試験片を温度：９５０℃の溶融塩（Na_2SO_4：２０ｗｔ％，ＮａＣｌ：５ｗｔ％，Na_2CO_3：７５ｗｔ％）に浸漬し、その後取り出して９００℃に保持した電気炉中に１５０時間保持したのち冷却した。この試験片を切断して断面のミクロ組織をＳＥＭ（走査型電子顕微鏡）で観察し、結晶粒界に沿って進行した平均侵食深さを求め、その結果を表４に示し、高温耐粒界腐食性を評価した。

【００３４】

【表４】

【００３２】得られた本発明柱状晶大型鋳物板１～１６＊

種　別		平均侵食深さ（μｍ）	種　別		平均侵食深さ（μｍ）
本発明柱状晶大型鋳物板	1	３４	本発明柱状晶大型鋳物板	11	４７
	2	８８		12	１５１
	3	８４		13	１２４
	4	１６７		14	１７５
	5	４８		15	９１
	6	１０５		16	５９
	7	６２	従来柱状晶大型鋳物板	17	７０１
	8	５７		18	５６０
	9	７０		19	４９８
	10	１８８		20	５４５

【００３５】　【発明の効果】表１～表４に示される結果から、本発明

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柱状晶大型鋳物板１～１６は、Ｚｒを多く含む従来柱状晶大型鋳物板１７～２０に比べて平均侵食深さが小さいところから、本発明柱状晶大型鋳物板１～１６は高温耐粒界腐食性に優れていることがわかる。従って、この発明の柱状晶Ｎｉ基耐熱合金大型鋳物は高温耐粒界腐食性＊

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＊に優れているところから、ガスタービンのタービン動・静翼および高温ブロアーの動翼として過酷な条件下で使用しても長期に亘って使用することができ、産業上すぐれた効果を奏するものである。

フロントページの続き

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